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(74) Agent: DEN HARTOG, Jeroen, Hendrikus, Joseph;  
DSM Patents & Trademarks, P.O. Box 9, NL-6160 MA  
Geleen (NL).

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(71) Applicants (for all designated States except US): DSM  
N.V. [NL/NL]; Het Overloon 1, NL-6411 TE Heerlen  
(NL). JSR CORPORATION [JP/JP]; JSR Building,  
2-11-24 Tsukiji, Chuo-ku, Tokyo 104-8410 (JP).

(72) Inventors; and

(75) Inventors/Applicants (for US only): UCHIDA, Hirofumi  
[JP/JP]; 2-5-4-1-402 Umezono, Tsukuba, Ibaraki 305-0045  
(JP). KOMIYA, Zen [JP/JP]; 2-18-33 MI-3 Umezono,  
Tsukuba Ibaraki 305-0045 (JP). UKACHI, Takashi  
[JP/JP]; 5-22-9, Komiya, Ushiku, Ibaraki 300-1216 (JP).

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(54) Title: OPTICAL FIBER COATING COMPOSITIONS

(57) Abstract: A coated optical fiber having an outer coating layer, being a cured coating from a liquid curable resin composition comprising: (A) a urethane (meth)acrylate obtained by the reaction of a polyol compound, a diisocyanate compound, and a hydroxyl group-containing (meth)acrylate compound, or a urethane (meth)acrylate obtained by the reaction of a diisocyanate compound and a hydroxyl group-containing (meth)acrylate compound, (B) a (meth)acrylate compound shown by the following formula (1),  $\text{CH}_2=\text{C}(\text{R}^1)\text{-COO-C}_n\text{H}_{2n+1}$  wherein  $\text{R}^1$  represents a hydrogen atom or a methyl group and  $n$  is an integer from 4 to 12, and (C) a polymerization initiator, wherein the cured products of the liquid curable resin composition has a modulus of elasticity of 50 Mpa or more.

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OPTICAL FIBER COATING COMPOSITIONS5 Field of the Invention

The present invention relates to a liquid curable resin composition capable of producing a cured material having excellent mechanical properties and surface characteristics suitable as an outer coating layer such as a secondary material and bundling material for optical fibers.

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Description of related art

In the manufacture of optical fibers, resin coatings are provided over glass fibers prepared by spinning a molten glass for protection and reinforcement. As such a resin coating, a structure consisting of a primary flexible coating layer formed on the surface of optical fibers and a secondary rigid coating layer applied thereon is known. Tape-shaped optical fibers and optical fiber cables comprising a number of fibers provided with these resin coatings bundled using bundling materials are also well known. Resin compositions for primary coating layers are called primary materials, for secondary coating layers are called secondary materials, and for bundling a number of optical fibers are called bundling materials. In addition, a material for further binding several tape-shaped optical fibers and optical fiber cables is also called a bundling material. These resin coatings are usually provided by curing a liquid curable resin composition applied on the surface of the optical fibers by using heat or light, in particular, ultraviolet rays.

Such a secondary material and bundling material must have high modulus of elasticity and excellent mechanical characteristics such as high breaking elongation. Optical fibers, tapes, and cables to which the secondary material or bundling material has been applied are wound around a bobbin, which is stored or transported with the secondary materials or the bundling materials being in contact with each other. For this reason, the secondary materials or the bundling materials must have superior surface characteristics to avoid adherence of these materials.

Accordingly, an object of the present invention is to provide a coated optical fiber having an outer coating layer, being a cured coating from a liquid curable resin composition capable of producing cured products having excellent

mechanical properties and surface characteristics.

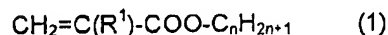
#### Summary of the invention

- As a result of extensive studies on liquid curable resin compositions satisfying the both requirements for excellent mechanical properties and surface characteristics, the present inventors have found that a cured material having high modulus of elasticity and breaking elongation, and at the same time, exhibiting superior surface characteristics with a small adhering force can be obtained from a liquid curable resin composition comprising a urethane (meth)acrylate oligomer and a (meth)acrylate compound having an alkyl group containing 4-12 carbons.

#### Detailed description of the invention

- Accordingly, an object of the present invention is to provide a coated optical fiber having an outer coating layer, being a cured coating from a liquid curable resin composition comprising:

- (A) a urethane (meth)acrylate obtained by the reaction of a polyol compound, a diisocyanate compound, and a hydroxyl group-containing (meth)acrylate compound, or a urethane (meth)acrylate obtained by the reaction of a diisocyanate compound and a hydroxyl group-containing (meth)acrylate compound,
- (B) a (meth)acrylate compound shown by the following formula (1),



- wherein  $\text{R}^1$  represents a hydrogen atom or a methyl group and  $n$  is an integer from 4 to 12, and
- (C) a polymerization initiator,
- wherein the cured products of the liquid curable resin composition have a modulus of elasticity of 50 MPa or more.

- The urethane (meth)acrylate of the component (A) which is a polymerizable oligomer can be obtained by reacting a polyol compound, a diisocyanate compound, and a hydroxyl group-containing (meth)acrylate compound, or by reacting a diisocyanate compound and a hydroxyl group-containing (meth)acrylate compound. Specifically, the component (A) can be

obtained by reacting the isocyanate group in the diisocyanate compound with the hydroxyl group in the polyol compound and/or hydroxyl group-containing (meth)acrylate compound.

5 In the preparation of urethane (meth)acrylate (A-1) from a polyol compound, diisocyanate compound, and hydroxyl group-containing (meth)acrylate, these compounds are preferably used in such proportions that the isocyanate group of the diisocyanate compound and the hydroxyl group of the hydroxyl group-containing (meth)acrylate are respectively 1.1-2 equivalents and 0.1-1 equivalent for 1 equivalent of the hydroxyl group of the polyether polyol. In the preparation of urethane (meth)acrylate (A-2) from a diisocyanate compound and hydroxyl group-containing (meth)acrylate, these compounds are preferably used in such a proportion that the isocyanate group of the diisocyanate compound and the hydroxyl group of the hydroxyl group-containing (meth)acrylate are equivalent.

15 In addition, it is possible to prepare both the urethane (meth)acrylate (A-1) and the urethane (meth)acrylate (A-2) at the same time by adjusting the amount of a polyol compound, polyisocyanate compound, and hydroxyl group-containing (meth)acrylate compound.

20 These reactions can be carried out, for instance, by a process of reacting the polyol compound, diisocyanate compound, and hydroxyl group-containing (meth)acrylate compound altogether; a process of reacting the polyol compound and diisocyanate compound, and reacting the resulting compound with the hydroxyl group-containing (meth)acrylate compound; a process of reacting the diisocyanate compound and hydroxyl group-containing (meth)acrylate compound, and reacting the resulting product with the polyol compound; and a process of reacting the diisocyanate compound and hydroxyl group-containing (meth)acrylate compound, reacting the resulting product with the polyol compound, and further reacting the hydroxyl group-containing (meth)acrylate compound.

30 As a diisocyanate compound which is used for the synthesis of urethane (meth)acrylate (A), an aromatic diisocyanate, alicyclic diisocyanate, aliphatic diisocyanate, and the like can be given. Examples of aromatic diisocyanates include 2,4-tolylene diisocyanate, 2,6-tolylene diisocyanate, 1,3-xylylene diisocyanate, 1,4-xylylene diisocyanate, 1,5-naphthalene diisocyanate, m-phenylene diisocyanate, p-phenylene diisocyanate, 3,3'-dimethyl-4,4'-diphenylmethane diisocyanate, 4,4'-diphenylmethane diisocyanate,

3,3'-dimethylphenylene diisocyanate, 4,4'-biphenylene diisocyanate, bis(2-isocyanateethyl)fumarate, 6-isopropyl-1,3-phenyl diisocyanate, 4-diphenylpropane diisocyanate, tetramethylxylylene diisocyanate, and the like. Examples of alicyclic diisocyanates include isophorone diisocyanate, methylenebis(4-cyclohexylisocyanate), hydrogenated diphenylmethane diisocyanate, hydrogenated xylylene diisocyanate, 2,5-bis(isocyanatemethyl)-bicyclo[2.2.1]heptane, 2,6-bis(isocyanatemethyl)-bicyclo[2.2.1]heptane, and the like. As examples of aliphatic diisocyanates, 1,6-hexane diisocyanate, 2,2,4-trimethylhexamethylene diisocyanate, lysine diisocyanate, and the like can be given. Of these, 2,4-tolylene diisocyanate and isophorone diisocyanate are particularly preferred. Aliphatic isocyanates such as IPDI are most preferred. These diisocyanates can be used either individually or in combinations of two or more.

As hydroxyl group-containing (meth)acrylate compounds used in the synthesis of the urethane (meth)acrylate (A), a hydroxyl group-containing (meth)acrylate containing a hydroxyl group bonded to a primary carbon atom (hereinafter designated as "(meth)acrylate containing a primary hydroxyl group") and a hydroxyl group-containing (meth)acrylate containing a hydroxyl group bonded to a secondary carbon atom (hereinafter designated as "(meth)acrylate containing a secondary hydroxyl group") are preferable. A hydroxyl group-containing (meth)acrylate containing a hydroxyl group bonded to a tertiary carbon atom (hereinafter designated as "(meth)acrylate containing a tertiary hydroxyl group") is not preferred because of its inferior reactivity with an isocyanate group.

Examples of the above (meth)acrylate containing a primary hydroxyl group include 2-hydroxyethyl (meth)acrylate, 4-hydroxybutyl (meth)acrylate, 1,6-hexanediol mono(meth)acrylate, pentaerythritol tri(meth)acrylate, dipentaerythritol penta(meth)acrylate, neopentyl glycol mono(meth)acrylate, trimethylolpropane di(meth)acrylate, trimethylolethane di(meth)acrylate, and (meth)acrylate of the following formula (2):



wherein  $\text{R}^2$  represents a hydrogen atom or a methyl group and  $m$  is an integer from 1 to 3.

Examples of the above (meth)acrylate containing a secondary hydroxyl group include 2-hydroxypropyl (meth)acrylate, 2-hydroxybutyl

(meth)acrylate, 2-hydroxy-1-phenyloxypropyl (meth)acrylate, 4-hydroxycyclohexyl (meth)acrylate, compounds obtained by the addition reaction of (meth)acrylic acid and glycidyl group-containing compounds such as alkyl glycidyl ether, allyl glycidyl ether, or glycidyl (meth)acrylate, and the like.

- 5                   As examples of polyols used for the preparation of the urethane (meth)acrylate (A), polyether diols such as aliphatic polyether diol, alicyclic polyether diol, and aromatic polyether diol, polyester diol, polycarbonate diol, polycaprolactone diol, and the like can be given. These polyols can be used either individually or in combinations of two or more. Polyols with a tri or more valence, 10 which are synthesized by reacting a diol compound and a polyisocyanate, can also be used as the above polyols. There are no specific limitations to a method of polymerizing the structural unit of these polyols. Random polymerization, block polymerization, or graft polymerization can be employed.

- As examples of the aliphatic polyether diols, polyethylene glycol, 15 polypropylene glycol, polytetramethylene glycol, polyhexamethylene glycol, polyheptamethylene glycol, polydecamethylene glycol, polyether diols obtained by ring-opening copolymerization of two or more of ion-polymerizable cyclic compounds, and the like can be given.

- As examples of the ion-polymerizable cyclic compounds, cyclic 20 ethers such as ethylene oxide, propylene oxide, butene-1-oxide, isobutene oxide, 3,3-bis(chloromethyl)oxetane, tetrahydrofuran, 2-methyltetrahydrofuran, 3-methyltetrahydrofuran, dioxane, trioxane, tetraoxane, cyclohexene oxide, styrene oxide, epichlorohydrin, glycidyl methacrylate, allyl glycidyl ether, allyl glycidyl carbonate, butadiene monoxide, isoprene monoxide, vinyl oxetane, vinyl 25 tetrahydrofuran, vinyl cyclohexene oxide, phenyl glycidyl ether, butyl glycidyl ether, and glycidyl benzoate can be given.

- As examples of the polyether diols obtained by ring-opening copolymerization of two or more of ion-polymerizable cyclic compounds, binary 30 polymers obtained by the ring-opening polymerization of the combinations of monomers such as tetrahydrofuran and propylene oxide, tetrahydrofuran and 2-methyltetrahydrofuran, tetrahydrofuran and 3-methyl tetrahydrofuran, tetrahydrofuran and ethylene oxide, propylene oxide and ethylene oxide, and butene-1-oxide and ethylene oxide, terpolymers obtained by the polymerization of the combinations of monomers such as tetrahydrofuran, butene-1-oxide, and 35 ethylene oxide, and the like can be given.

                  Moreover, polyether diols obtained by ring-opening

copolymerization of the above ion-polymerizable cyclic compounds and cyclic imines such as ethyleneimine, cyclic lactones such as  $\beta$ -propyolactone and lactideglycolic acid, or dimethylcyclopolsiloxanes can also be used as the above polyether diols.

- 5                   Examples of commercially available products of the aliphatic polyether diols include PTMG650, PTMG1000, PTMG2000 (manufactured by Mitsubishi Chemical Corp.), PPG400, PPG1000, EXCENOL720, 1020, 2020 (manufactured by Asahi Oline Co., Ltd.), PEG1000, UNISAFE DC1100, DC1800 (manufactured by Nippon Oil and Fats Co., Ltd.), PPTG2000, PPTG1000, 10 PTG400, PTGL2000 (manufactured by Hodogaya Chemical Co., Ltd.), Z-3001-4, Z-3001-5, PBG2000A, PBG2000B, EO/BO4000, EO/BO2000 (manufactured by Dai-ichi Kogyo Seiyaku Co., Ltd.), and the like.

- 15                   As examples of alicyclic polyether diols, alkylene oxide addition diol of hydrogenated bisphenol A, alkylene oxide addition diol of hydrogenated bisphenol F, alkylene oxide addition diol of 1,4-cyclohexane diol, and the like can be given.

- 20                   Examples of aromatic polyether diols include alkylene oxide addition diol of bisphenol A, alkylene oxide addition diol of bisphenol F, alkylene oxide addition diol of hydroquinone, alkylene oxide addition diol of naphthohydroquinone, alkylene oxide addition diol of anthrahydroquinone, and the like. Commercially available products such as UniolDA400, DA700, DA1000, and DA4000 (manufactured by Nippon Oil and Fats Co., Ltd.) can be used as the aromatic polyether diols.

- 25                   Examples of polyester diols include polyester diols obtained by reacting a polyhydric alcohol and a polybasic acid, and the like. Examples of the polyhydric alcohol include ethylene glycol, polyethylene glycol, propylene glycol, polypropylene glycol, tetramethylene glycol, polytetramethylene glycol, 1,6-hexanediol, neopentyl glycol, 1,4-cyclohexanedimethanol, 3-methyl-1,5-pentanediol, 1,9-nonanediol, 2-methyl-1,8-octanediol, and the like. As examples of 30 the polybasic acid, phthalic acid, isophthalic acid, terephthalic acid, maleic acid, fumaric acid, adipic acid, sebacic acid, and the like can be given.

- 35                   As examples of commercially available products of the above polyester diols, Kurapol P-2010, P-1010, L-2010, L-1010, A-2010, A-1010, F-2020, F-1010, PMIPA-2000, PKA-A, PNOA-2010, PNOA-1010 (manufactured by Kuraray Co., Ltd.), and the like can be given.

As examples of the polycarbonate diols, polycarbonate of

polytetrahydrofuran, polycarbonate of 1,6-hexanediol, and the like, and commercially available products such as DN-980, 981, 982, 983 (manufactured by Nippon Polyurethane Industry Co., Ltd.), PC-8000 (manufactured by PPG), and PC-THF-CD (manufactured by BASF) can be given.

5                   As examples of polycaprolactone diols, polycaprolactone diols obtained by reacting  $\epsilon$ -caprolactone and a diol, and the like can be given. Examples of such diols used for the reaction with  $\epsilon$ -caprolactone include ethylene glycol, polyethylene glycol, propylene glycol, polypropylene glycol, tetramethylene glycol, polytetramethylene glycol,

10   1,2-polybutylene glycol, 1,6-hexanediol, neopentyl glycol, 1,4-cyclohexanedimethanol, 1,4-butanediol, and the like. These polycaprolactone diols are commercially available under the trademarks of PLACCEL205, 205AL, 212, 212AL, 220, 220AL (manufactured by Daicel Chemical Industries, Ltd.), and the like.

15                   Examples of polyols other than the above-mentioned polyols include ethylene glycol, propylene glycol, 1,4-butanediol, 1,5-pentane diol, 1,6-hexanediol, neopentyl glycol, 1,4-cyclohexanedimethanol, hydrogenated bisphenol A, hydrogenated bisphenol F, dimethylol compound of dicyclopentadiene, tricyclodecanedimethanol, pentacyclodecanedimethanol,  $\epsilon$ -methyl- $\epsilon$ -valerolactone, polybutadiene with a terminal hydroxyl group,

20   hydrogenated polybutadiene with a terminal hydroxyl group, castor oil-modified polyol, polydimethylsiloxane compounds with terminal diols, polydimethylsiloxane carbitol-modified polyol, and the like.

                  It is possible to use a diamine together with a polyether polyol in

25   the synthesis of the urethane (meth)acrylate (A). Examples of such a diamine include ethylenediamine, tetramethylenediamine, hexamethylenediamine, p-phenylenediamine, 4,4'-diaminodiphenylmethane, diamines containing a heteroatom, polyether diamines, and the like.

                  Part of the (meth)acrylates containing a hydroxyl group can be

30   replaced by the compounds having a functional group which can be added to an isocyanate group. For example,  $\gamma$ -aminopropyltriethoxysilane,  $\gamma$ -mercaptopropyltrimethoxy-silane, and the like can be used. Use of these compounds improves adhesion to substrates such as glass.

                  In the synthesis of the urethane (meth)acrylate (A), it is desirable

35   to use a urethanization catalyst, such as copper naphthenate, cobalt naphthenate, zinc naphthenate, dibutyltin dilaurate, triethylamine, 1,4-diazabicyclo[2.2.2]octane,



or 2,6,7-trimethyl-1,4-diazabicyclo[2.2.2]octane, in the amount from 0.01 to 1 wt% of the total amount of reactants. In addition, such reactions are carried out usually at 5-90°C, and preferably at 10-80°C.

5 The urethane (meth)acrylate (A) used in the present invention has a polystyrene-reduced molecular weight measured by the gel permeation chromatography in the range of 500-20,000, and preferably 700-15,000. If the molecular weight is less than 500, the cured products may have only a small breaking elongation; if more than 20,000, on the other hand, the resin composition may have unduly high viscosity.

10 The amount of the urethane (meth)acrylate (A) in the liquid curable resin composition of the present invention is preferably 30-90 wt%, more preferably 55-87 wt%, and particularly preferably 65-85 wt%. If less than 30 wt%, the modulus of elasticity largely depends upon temperatures; if more than 90 wt%, the liquid curable resin composition may have unduly high viscosity.

15 Given as examples of the component (B) in the liquid curable resin composition of the present invention, which is the (meth)acrylate compound shown by the formula (1), are butyl (meth)acrylate, isobutyl (meth)acrylate, t-butyl (meth)acrylate, pentyl (meth)acrylate, amyl (meth)acrylate, isoamyl (meth)acrylate, hexyl (meth)acrylate, heptyl (meth)acrylate, octyl (meth)acrylate, 20 2-ethylhexyl (meth)acrylate, iso-octyl (meth)acrylate, nonyl (meth)acrylate, isononyl (meth)acrylate, decyl (meth)acrylate, iso-decyl (meth)acrylate, undecyl (meth)acrylate, dodecyl (meth)acrylate, and lauryl (meth)acrylate. Of these (meth)acrylate compounds, the compounds having an integer 8, 9 or 10 for n in the formula (1) are preferred in view of processability. Most preferred are n=8 or 9. 25 A particularly preferred (meth)acrylate compound in view of low viscosity is 2-ethylhexyl acrylate having an integer 8 for n in the formula (1), and isodecylacrylate, having an integer 10 for n; another preferred compound is octyldecylacrylate.

30 The proportion of the (meth)acrylate compound (B) in the liquid curable resin composition of the present invention is preferably 1-60 wt%, and more preferably 3-30 wt%. If less than 1 wt%, the effect of improvement in the mechanical properties and surface characteristics is insufficient; if more than 60 wt%, volatility of the resin composition is unacceptably high.

35 As the polymerization initiators (C) in the liquid curable resin composition of the present invention, either a heat polymerization initiator or a photopolymerization initiator can be used; photopolymerisation is strongly

preferred because of cure speed.

If the liquid curable resin composition of the present invention is cured by heat, a heat polymerization initiator such as a peroxide or azo compound can usually be used. Specific examples include benzoyl peroxide, t-butyloxy benzoate, azobisisobutyronitrile, and the like.

If the liquid curable resin composition of the present invention is cured by irradiation of lights, a photopolymerization initiator is used. Optionally, a photosensitizer can also be added. Given as examples of the photopolymerization initiator are 1-hydroxycyclohexyl phenyl ketone, 2,2-dimethoxy-2-

10 phenylacetophenone, xanthone, fluorenone, benzaldehyde, fluorene, anthraquinone, triphenylamine, carbazole, 3-methylacetophenone, 4-chlorobenzophenone, 4,4'-dimethoxybenzophenone, 4,4'-diamino-benzophenone, Michler's ketone, benzoin propyl ether, benzoin ethyl ether, benzyl methyl ketal, 1-(4-isopropylphenyl)-2-hydroxy-2- methylpropan-1-one, 15 2-hydroxy-2-methyl-1-phenylpropan-1-one, thioxanethone, diethylthioxanthone, 2- isopropylthioxanthone, 2-chlorothioxanthone, 2-methyl-1-[4-(methylthio)phenyl]-2-morpholino-propan-1-one, 2,4,6-trimethylbenzoyl diphenylphosphine oxide, bis-(2,6-dimethoxybenzoyl)-2,4,4-trimethylpentylphosphine oxide; IRGACURE 184, 369, 651, 500, 907, CGI 1700, CGI 1750, CGI 1850, CG24-61, Darocur 20 1116, 1173 (manufactured by Ciba Specialty Chemicals Co.); Lucirin LR8728 (manufactured by BASF); and Ubecryl P36 (manufactured by UCB). Examples of photosensitizers include triethylamine, diethylamine, N-methyldiethanoleamine, ethanolamine, 4-dimethylaminobenzoic acid, 4-methyl dimethylaminobenzoate, 4-ethyl dimethylaminobenzoate, 4-isoamyl dimethylaminobenzoate; Ubecryl P102, 25 103, 104, 105 (manufactured by UCB); and the like.

The proportion of the polymerization initiator (C) used in the liquid curable composition of the present invention is preferably 0.1-10 wt%, and more preferably 0.3-7 wt%.

In addition to the above components, a polymerizable 30 unsaturated monomer (D) other than the (meth)acrylate compound (B) may be added to increase curability and adjust the viscosity of the liquid curable resin composition of the present invention in the amount of 0-60 wt%, and preferably 3-40 wt%. If more than 60 wt% of the component (D) is added, temperature dependency of the modulus of elasticity of the cured products may increase.

35 Mono-functional compounds and poly-functional compounds are given as examples of the polymerizable unsaturated monomer (D). Given as

examples of monofunctional compounds are vinyl group-containing lactam such as N-vinylpyrrolidone and N-vinylcaprolactam, alicyclic structure-containing (meth)acrylates such as isobornyl (meth)acrylate, bornyl (meth)acrylate, tricyclodecanyl (meth)acrylate, dicyclopentanyl (meth)acrylate, dicyclopentenyl (meth)acrylate, and cyclohexyl (meth)acrylate, benzyl (meth)acrylate, 4-butylcyclohexyl (meth)acrylate, acryloylmorpholine, vinylimidazole, vinylpyridine, and the like. In addition to the above compounds, 2-hydroxyethyl (meth)acrylate, 2-hydroxypropyl (meth)acrylate, 4-hydroxybutyl (meth)acrylate, stearyl (meth)acrylate, iso-stearyl (meth)acrylate, tetrahydrofurfuryl (meth)acrylate, polyethylene glycol mono(meth)acrylate, polypropylene glycol mono(meth)acrylate, methoxyethylene glycol (meth)acrylate, ethoxyethyl (meth)acrylate, methoxypolyethylene glycol (meth)acrylate, methoxy polypropylene glycol (meth)acrylate, diacetone (meth)acrylamide, isobutoxymethyl (meth)acrylamide, N,N-dimethyl (meth)acrylamide, t-octyl (meth)acrylamide, dimethylaminoethyl (meth)acrylate, diethylaminoethyl (meth)acrylate, 7-amino-3,7-dimethyloctyl (meth)acrylate, N,N-diethyl (meth)acrylamide, N,N-dimethylamino propyl (meth)acrylamide, hydroxybutyl vinyl ether, lauryl vinyl ether, cetyl vinyl ether, 2-ethylhexyl vinyl ether, and the like can be given.

As examples of commercially available products of the monofunctional compound used as the polymerizable unsaturated monomer, ARONIX M-111, M-113, M-114, M-117 (manufactured by Toagosei Co., Ltd.), KAYARAD TC110S, R629, R644 (manufactured by Nippon Kayaku Co., Ltd.), IBXA, Viscoat3700 (manufactured by Osaka Organic Chemical Industry, Ltd.), and the like can be given.

Examples of polyfunctional compounds include trimethylolpropane tri(meth)acrylate, pentaerythritol tri(meth)acrylate, ethylene glycol di(meth)acrylate, tetraethylene glycol di(meth)acrylate, polyethylene glycol di(meth)acrylate, 1,4-butanediol di(meth)acrylate, 1,6-hexanediol di(meth)acrylate, neopentyl glycol di(meth)acrylate, trimethylolpropanetrioxoethyl (meth)acrylate, tris(2-hydroxyethyl)isocyanurate tri(meth)acrylate, tris(2-hydroxyethyl)isocyanurate di(meth)acrylate, tricyclodecanedimethanol di(meth)acrylate, di(meth)acrylate of diol of ethylene oxide or propylene oxide adduct of bisphenol A, di(meth)acrylate of diol of ethylene oxide or propylene oxide adduct of hydrogenated bisphenol A, epoxy(meth)acrylate obtained by the addition of (meth)acrylate to diglycidyl ether of bisphenol A, triethylene glycol divinyl ether, and the like. Examples of commercially available products of the above polyfunctional compounds include

Yupimer UV SA1002, SA2007 (manufactured by Mitsubishi Chemical Corp.),  
Viscoat 700 (manufactured by Osaka Organic Chemical Industry, Ltd.), KAYARAD  
R-604, DPCA-20, DPCA-30, DPCA-60, DPCA-120, HX-620, D-310, D-330  
(manufactured by Nippon Kayaku Co., Ltd.), ARONIX M-210, M-215, M-315, M-  
5 325 (manufactured by Toagosei Co., Ltd.), and the like.

Various additives such as antioxidants, coloring agents, UV  
absorbers, light stabilizers, silane coupling agents, heat polymerization inhibitors,  
leveling agents, surfactants, preservatives, plasticizers, lubricants, solvents, fillers,  
aging preventives, wettability improvers, and coating surface improvers can also  
10 be added in addition to the above components, as required. As examples of the  
antioxidants, Irganox 1010, 1035, 1076, 1222 (manufactured by Ciba Specialty  
Chemicals Co., Ltd.), Antigene P, 3C, FR, GA-80, (manufactured by Sumitomo  
Chemical Industries Co., Ltd.), and the like can be given. As examples of the UV  
absorbers, Tinuvin P, 234, 320, 326, 327, 328, 329, 213 (manufactured by Ciba  
15 Specialty Chemicals Co., Ltd.), Seesorb 102, 103, 110, 501, 202, 712, 704  
(manufactured by Shipro Kasei K.K.), and the like can be given. As examples of  
the light stabilizers, Tinuvin 292, 144, 622LD (manufactured by Ciba Specialty  
Chemicals Co., Ltd.), Sanol LS770 (manufactured by Sankyo Co., Ltd.), TM-061  
(manufactured by Sumitomo Chemical Co., Ltd.), and the like can be given. As  
20 examples of the silane coupling agents,  $\gamma$ -aminopropyltriethoxysilane,  $\gamma$ -  
mercaptopropyltrimethoxy-silane,  $\gamma$ -methacryloxypropyltrimethoxysilane, and the  
like, and commercially available products such as SH6062, 6030 (manufactured  
by Dow Corning Toray Silicone Co., Ltd.), and KBE903, 603, 403 (manufactured  
by Shin-Etsu Chemical Co., Ltd.) can be given.

25 Furthermore, other oligomers and polymers, as well as other  
additives can optionally be added to the liquid curable resin composition of the  
present invention inasmuch as characteristics of the composition of the present  
invention are not impaired.

Examples of such other oligomers and polymers include  
30 polyester (meth)acrylate, epoxy (meth)acrylate, polyamide (meth)acrylate,  
siloxane polymers having a (meth)acryloyloxy group, glycidyl methacrylate, and  
the like.

The composition of the present invention is cured by heat or  
radiation. Radiation used herein includes infrared rays, visible rays, ultraviolet  
35 rays, X-rays, electron beams,  $\alpha$ -rays,  $\beta$ -rays,  $\gamma$ -rays, and the like. Particularly  
preferred radiation is ultraviolet rays.

In view of ensuring excellent handling properties and applicability, the viscosity of the liquid curable resin composition of the present invention is in the range of 0.1-10 Pa·s, preferably 1-8 Pa·s, and particular preferably 2-6 Pa·s.

5 Cured materials made from the resin composition of the present invention have high modulus of elasticity and breaking elongation, and at the same time, exhibit superior surface characteristics with a small adhering force. Therefore, the resin composition is useful as a secondary material or bundling material for optical fibers. The cured material must have modulus of elasticity of at  
10 least 50 MPa, preferably more than 200 MPa, and particularly preferably more than 400 MPa. If the modulus of elasticity is less than 50 MPa, an attenuation loss of the optical fiber may be too large to serve the product to the above-mentioned application. In addition, the cured product preferably has breaking elongation of 20% or more, preferably 25% or more, and more preferably 30% or more. If the  
15 breaking elongation is less than 20%, optical fibers may be more easily broken. Moreover, the cured products preferably have a water absorption rate of 3% or less, preferably 2.7% or less, and more preferably 2.4% or less. If the water absorption rate is more than 3%, the transmission loss may increase when the optical fiber is dipped in warm water.

20 A film adhering force is a particularly important characteristic because optical fibers are stored or transported under the conditions in which secondary materials or bundling materials are in contact with each other. For this reason, film adhering force preferably is 0.09 N/cm or less, preferably 0.08 N/cm or less, and more preferably 0.07 N/cm or less.

25 The present invention will be explained in more detail by examples, which are not intended to be limiting of the present invention.

### Preparation Example 1

#### Synthesis example of urethane (meth)acrylate

A reaction vessel equipped with a stirrer was charged with polypropylene glycol having a number average molecular weight of 3200 (402.9 g), tolylene diisocyanate (263.9 g), 2,6-di-t-butyl-p-cresol (0.24 g), and phenothiazine (0.08 g). The mixture was cooled to 15°C while stirring. After the addition of dibutyl tin dilaurate (0.8 g), 2-hydroxypropyl acrylate (87.9 g) was added dropwise while controlling the temperature to less than 30°C. After the addition, the mixture was stirred for one hour at 40°C. Next, 2-hydroxyethyl acrylate (244.2 g) was added dropwise while controlling the temperature to less than 60°C. After the addition, the mixture was stirred at 60°C. The reaction was terminated when the residual isocyanate was 0.1 wt% or less. The urethane (meth)acrylate oligomer thus obtained is designated as "Polymerizable oligomer (a)".

#### Examples 1-2 and Comparative Example A-B

A reaction vessel equipped with a stirrer was charged with the compounds listed in Table 1 in the proportion shown in Table 1. The mixture was stirred at 50°C to produce a homogeneous solution, thus obtaining the compositions of Examples and Comparative Examples. Mechanical properties, viscosity, and surface characteristic of the resulting cured products were evaluated according to the following methods. Results are shown in Table 1.

#### (1) Measuring method of viscosity

The viscosity at 25°C of the compositions obtained in Examples and Comparative Examples was measured. Viscometer B8H-BII manufactured by Tokimeck Co., Ltd. was used for the viscosity measurement.

#### (2) Measuring methods of modulus of elasticity and breaking elongation

Modulus of elasticity and breaking elongation of the cured products obtained from the compositions of Examples and Comparative Examples were measured. The liquid compositions were applied to a glass plate using an applicator with a thickness of 381 µm, irradiated by ultraviolet rays by using a 3.5 kW metal halide lamp ("SMX-3500/F-OS", manufactured by ORC Co., Ltd.) at a dose of 1.0 J/cm<sup>2</sup> in air to form cured coatings having a thickness of about 200 µm. Test specimens for measurement of modulus of elasticity and breaking

elongation were obtained by cutting the cured films into strips with a width of 0.6 cm. The modulus of elasticity and breaking elongation were measured according to JIS K7127 using the test specimens thus obtained. The measurement was carried out at a bench mark distance of 25 mm, a temperature of 23°C, and a humidity of 50%RH. Drawing rates of 1 mm/min and 50 mm/min were adopted respectively for measurement of modulus of elasticity and breaking elongation.

### (3) Evaluation method for surface characteristics

An adhering force between cured films obtained in Examples and Comparative Examples were measured to evaluate the surface characteristics. The liquid compositions were applied to a glass plate using an applicator with a thickness of 127 µm, irradiated by ultraviolet rays by using a 3.5 kW metal halide lamp ("SMX-3500/F-OS", manufactured by ORC Co., Ltd.) at a dose of 1.0 J/cm<sup>2</sup> in air to form cured coatings having a thickness of about 70 µm. The cured film was divided into two pieces, which were immediately caused to adhere with the upper surfaces (the surfaces which had been in contact with air) face-to-face. The adhered films were conditioned at 23°C and 50% RH for 24 hours, and cut into strips with a width of 1 cm to obtain test specimens for measuring adhering force. The adhered films were held with upper and lower chucks of a tensile machine and peeled at a tensile rate of 50 mm/min. to measure the force required for the films to be peeled. The measurement was carried out at a temperature of 23°C and a relative humidity of 50%. The smaller the adhesion force, the better the surface characteristics.

### (4) Measuring method of water absorption

The water absorption rate of the cured materials made from the compositions obtained in Examples and Comparative Examples was measured. The liquid compositions were applied to a glass plate using an applicator with a thickness of 381 µm, irradiated by ultraviolet rays by using a 3.5 kW metal halide lamp ("SMX-3500/F-OS", manufactured by ORC Co., Ltd.) at a dose of 1.0 J/cm<sup>2</sup> in air to form cured coatings having a thickness of about 200 µm. The cured film was cut into pieces having a weight of about 1 g each and dried at 50°C under reduced pressure for 24 hours, before measuring the weight (W1). Next, the cured film pieces were dipped in water at 23°C for 24 hours, followed by measurement of the weight (W2). The cured film pieces were dried at 50°C under reduced pressure for 24 hours, then the weight (W3) was measured. The water absorption

rate was determined according to the following formula (1).

$$\text{Water absorption (\%)} = 100 \times (W2 - W3)/W1$$

The components shown in Table 1 are as follows.

- 5 Irgacure 651 and Irgacure 907: Photopolymerization initiator (manufactured by Ciba Specialty Chemicals Co.)  
Irganox 1035: Antioxidant (manufactured by Ciba Specialty Chemicals Co.)

[Table 1]

	Example		Comparative Example	
	1	2	A	B
Component				
Polymerizable oligomer (a)	78.2	78.2	78.2	78.2
2-Ethylhexyl acrylate	10	15	-	-
N-vinylcaprolactam	5.0	5.0	5.0	5.0
Isobornyl acrylate	6.8	1.8	16.8	1.8
Trimethylolpropane triacrylate	-	-	-	15
Irgacure 651	1.7	1.7	1.7	1.7
Irgacure 907	0.4	0.4	0.4	0.4
Irganox 1035	0.3	0.3	0.3	0.3
Total	102.4	102.4	102.4	102.4
Evaluation items				
Viscosity (Pa·s)	4.5	3.3	8.5	15
Modulus of elasticity (MPa)	520	460	750	970
Breaking elongation (%)	46	36	40	23
Film adhering force (N/cm)	0.07	0.06	0.14	0.10
Water absorption (%)	2.3	2.2	2.3	2.5

10

As can be seen from Table 1, the liquid curable resin compositions comprising a urethane (meth)acrylate oligomer (A), C<sub>4</sub>-C<sub>12</sub> alkyl (meth)acrylate (B), and polymerization initiator exhibit excellent bundling properties and produce cured products having not only high modulus of elasticity and breaking elongation, but also superior surface characteristics with small adhering force.

15



CLAIMS

1. Coated optical fiber comprising an outer coating layer being a cured coating from a liquid curable resin composition comprising:
- 5 (A) a urethane (meth)acrylate obtained by the reaction of a polyol compound, a diisocyanate compound, and a hydroxyl group-containing (meth)acrylate compound, or a urethane (meth)acrylate obtained by the reaction of a diisocyanate compound and a hydroxyl group-containing (meth)acrylate compound,
- 10 (B) a (meth)acrylate compound shown by the following formula (1),
- $$\text{CH}_2=\text{C}(\text{R}^1)-\text{COO}-\text{C}_n\text{H}_{2n+1} \quad (1)$$
- wherein  $\text{R}^1$  represents a hydrogen atom or a methyl group and  $n$  is an integer from 4 to 12, and
- 15 (C) a polymerization initiator, wherein the cured coating of the liquid curable resin composition has a modulus of elasticity of 50 MPa or more at 23°C.
2. The coated optical fiber according to claim 1, wherein the integer  $n$  in the formula (1) is 8, 9 or 10.
- 20 3. The coated optical fiber according to claim 2, wherein the component (B) is 2-ethylhexyl acrylate, octyl-decylacrylate or isodecylacrylate.
4. The coated optical fiber according to any one of claims 1-3, further comprising a component (D) which is a polymerizable unsaturated monomer other than the component (B).
- 25 5. The coated optical fiber according to any one of claims 1 to 4, of which the cured products have modulus of elasticity of 200 MPa or more.
6. A coated optical fiber according to any one of claims 1 to 5, in which the cured coating has a breaking elongation of 30% or more.
- 30 7. A coated optical fiber according to any one of claims 1 to 6, in which the cured coating has an adhering force of 0.08 N/cm or less.
8. A coated optical fiber according to any one of claims 1 to 7 wherein the outer coating is a secondary material or a bundling material for optical fibers.

# INTERNATIONAL SEARCH REPORT

International Application No

PCT/NL 00/00944

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C03C25/10 C09D175/16 C08F283/00

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C03C C09D C08G C08F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 536 529 A (SHUSTACK PAUL J) 16 July 1996 (1996-07-16) examples I-V ---	1-8
X	EP 0 565 798 A (BORDEN INC) 20 October 1993 (1993-10-20) examples I-V ---	1-8
X	US 5 146 531 A (SHUSTACK PAUL J) 8 September 1992 (1992-09-08) examples I-V ---	1-8
X	US 5 352 712 A (SHUSTACK PAUL J) 4 October 1994 (1994-10-04) examples I-V ---	1-8
	-/--	



Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

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Name and mailing address of the ISA

European Patent Office, P.B. 5618 Patentlaan 2  
NL - 2280 HV Rijswijk  
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,  
Fax: (+31-70) 340-3016

Authorized officer

Somann, K

# INTERNATIONAL SEARCH REPORT

International Application No

PCT/NL 00/00944

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 199 098 A (NOLAN KELLY J ET AL) 30 March 1993 (1993-03-30) example ---	1-8
X	US 5 538 791 A (SHUSTACK PAUL J) 23 July 1996 (1996-07-23) column 7, line 31 -column 67 column 9, line 16 - line 22 examples I,IV,IX,X ---	1-8
X	EP 0 566 801 A (BORDEN INC) 27 October 1993 (1993-10-27) examples I,IV,IX,X ---	1-8
X	US 5 587 403 A (SHUSTACK PAUL J) 24 December 1996 (1996-12-24) examples I,IV,IX,X ---	1-8
X	WO 98 19189 A (BORDEN INC ;SHUSTACK PAUL J (US)) 7 May 1998 (1998-05-07) examples 2,5,7,8 claim 13 ---	1-8
X	US 5 336 563 A (COADY CLIVE J ET AL) 9 August 1994 (1994-08-09) table I example 1 ---	1-8
X	US 5 219 896 A (COADY CLIVE J ET AL) 15 June 1993 (1993-06-15) example 1; table I -----	1-8

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/NL 00/00944

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
US 5536529	A	16-07-1996	US 5352712 A	04-10-1994
			US 5146531 A	08-09-1992
			US 5639846 A	17-06-1997
			AT 162163 T	15-01-1998
			CA 2082613 A	17-10-1993
			DE 69224059 D	19-02-1998
			DE 69224059 T	10-06-1998
			DK 565798 T	02-03-1998
			EP 0565798 A	20-10-1993
			EP 0745570 A	04-12-1996
			ES 2111054 T	01-03-1998
			GR 3026442 T	30-06-1998
			JP 5306147 A	19-11-1993
			CA 1321671 A	24-08-1993
			JP 8059302 A	05-03-1996
EP 0565798	A	20-10-1993	US 5352712 A	04-10-1994
			AT 162163 T	15-01-1998
			CA 2082613 A	17-10-1993
			DE 69224059 D	19-02-1998
			DE 69224059 T	10-06-1998
			DK 565798 T	02-03-1998
			EP 0745570 A	04-12-1996
			ES 2111054 T	01-03-1998
			GR 3026442 T	30-06-1998
			JP 5306147 A	19-11-1993
			US 5536529 A	16-07-1996
			US 5639846 A	17-06-1997
US 5146531	A	08-09-1992	US 5536529 A	16-07-1996
			US 5639846 A	17-06-1997
			US 5352712 A	04-10-1994
			CA 1321671 A	24-08-1993
			JP 8059302 A	05-03-1996
US 5352712	A	04-10-1994	US 5146531 A	08-09-1992
			AT 162163 T	15-01-1998
			CA 2082613 A	17-10-1993
			DE 69224059 D	19-02-1998
			DE 69224059 T	10-06-1998
			DK 565798 T	02-03-1998
			EP 0565798 A	20-10-1993
			EP 0745570 A	04-12-1996
			ES 2111054 T	01-03-1998
			GR 3026442 T	30-06-1998
			JP 5306147 A	19-11-1993
			US 5536529 A	16-07-1996
			US 5639846 A	17-06-1997
			CA 1321671 A	24-08-1993
			JP 8059302 A	05-03-1996
US 5199098	A	30-03-1993	NONE	
US 5538791	A	23-07-1996	US 5527835 A	18-06-1996
			US 5587403 A	24-12-1996
			AT 175175 T	15-01-1999
			CA 2082614 A	25-10-1993
			DE 69228052 D	11-02-1999

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/NL 00/00944

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 5538791 A		DE 69228052 T DK 566801 T EP 0566801 A ES 2125885 T GR 3029633 T JP 5306146 A	20-05-1999 06-09-1999 27-10-1993 16-03-1999 30-06-1999 19-11-1993
EP 0566801 A	27-10-1993	AT 175175 T CA 2082614 A DE 69228052 D DE 69228052 T DK 566801 T ES 2125885 T GR 3029633 T JP 5306146 A US 5527835 A US 5538791 A US 5587403 A	15-01-1999 25-10-1993 11-02-1999 20-05-1999 06-09-1999 16-03-1999 30-06-1999 19-11-1993 18-06-1996 23-07-1996 24-12-1996
US 5587403 A	24-12-1996	US 5538791 A US 5527835 A AT 175175 T CA 2082614 A DE 69228052 D DE 69228052 T DK 566801 T EP 0566801 A ES 2125885 T GR 3029633 T JP 5306146 A	23-07-1996 18-06-1996 15-01-1999 25-10-1993 11-02-1999 20-05-1999 06-09-1999 27-10-1993 16-03-1999 30-06-1999 19-11-1993
WO 9819189 A	07-05-1998	US 5744514 A AU 4910997 A BR 9706893 A CA 2250305 A EP 0895606 A JP 2000504435 T NO 982951 A	28-04-1998 22-05-1998 20-07-1999 07-05-1998 10-02-1999 11-04-2000 26-08-1998
US 5336563 A	09-08-1994	US 5219896 A AT 148132 T AU 635568 B AU 6435890 A DE 69029806 D DE 69029806 T DK 490981 T EP 0490981 A JP 3051163 B JP 5502466 T WO 9103499 A	15-06-1993 15-02-1997 25-03-1993 08-04-1991 06-03-1997 04-09-1997 28-07-1997 24-06-1992 12-06-2000 28-04-1993 21-03-1991
US 5219896 A	15-06-1993	US 5336563 A AT 148132 T AU 635568 B AU 6435890 A DE 69029806 D DE 69029806 T DK 490981 T	09-08-1994 15-02-1997 25-03-1993 08-04-1991 06-03-1997 04-09-1997 28-07-1997

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/NL 00/00944

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 5219896 A		EP 0490981 A	24-06-1992
		JP 3051163 B	12-06-2000
		JP 5502466 T	28-04-1993
		WO 9103499 A	21-03-1991
<hr/>			

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